The Nature of Carbon-Oxygen Complexes Produced by Different Oxidants: Towards a Unified Theory of Gasification?

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Introduction

There have been relatively few studies directly comparing the nature of surface carbon-oxygen complexes produced by the oxidation of carbon by different oxidizing agents. However, such studies as there are suggest, for the most part, a strong similarity between the chemical nature of such complexes, thereby potentially providing a unifying basis for the gasification of carbon by oxidizing species. In one such study, Marchon *et al.* [1] chemisorbed O_2, CO_2 and H_2O onto polycrystalline graphite at different temperatures, performed linear temperature programmed desorption (TPD) at a heating rate of 50 K/min, and compared the resulting desorption spectra. The principal TPD features were large CO desorption peaks at 973, 1093 and 1253K. They tentatively assigned these features to semi-quinone functional groups. It was concluded that the activation energy for adsorption was determined by the local surface environment of the group, the surface coverage, and the nature of the adsorbing molecule itself. Marchon *et al.* [1] also proposed a general mechanism of gasification, in which oxidizing species with the general formula RO, formed a semi-quinone group which could either be desorbed as CO or could be further oxidized to give a CO_2-producing lactone group. While generally plausible, this mechanism still leaves open the question of why one oxidizing agent should be more reactive than another for a particular carbon; e.g., why oxygen should be more reactive than NO, which is, in turn, more reactive than CO_2, when compared at the same gas phase concentration and temperature.

The present paper has two principal objectives: to further test the theory of the universal nature of oxygen complexes by comparing the TPD spectra of a char oxidized in O_2, CO_2, NO, HNO_3 and H_2O_2; and the reactivity question, which is approached by analysing TPD data, and reactivity and surface area measurements for a gasified char.

Experimental

The TPD apparatus has been described previously [2]. A heating rate of 100K/min was used in the current work because this yielded reasonable gas evolution rates and peak resolution. The carrier gas was ultra-high purity helium, and the typical TPD sample size was 10 mg. The results are presented with arbitrary rate and total gas units, but the scales are directly comparable from one graph to another. Char produced from Pittsburgh # 8 coal, obtained from the Argonne Premium Coal Sample Bank, was used in this set of experiments, because this coal goes through a fluid phase on carbonisaton in which most of the original porosity is lost. Therefore, essentially all the porosity is developed via gasification. The nitrogen BET surface area of the ungasified char resulting from heat treatment at 1273K for 2 hours was 3 m^2/g.

Oxidation by the gaseous oxidants and reactivity measurements were made in a TGA in the corresponding atmosphere at 0.1MPa. O_2 and CO_2 gasification were conducted in flowing gas, and NO gasification in a batch mode. Oxidations by HNO_3 were performed by stirring the char in a 15N solution at room temperature for 15 min. The same procedure was followed for H_2O_2 in a 30% solution. Nitrogen surface areas were determined from adsorption at 77K in a flow BET apparatus. Where appropriate, CO_2 surface areas were determined at 195K. No attempt was made to collect gaseous products of gasification during oxidation, so the total extents of oxidation by the different methods cannot be computed.

Results and Discussion

The TPD spectra for Pittsburgh # 8 coal char oxidized by O_2, CO_2, NO, HNO_3 and H_2O_2 are shown in Figures 1 through 5, respectively. As can be seen, there are certain features that are common to all the spectra, with two desorption peaks for CO_2 at about 600K and 920K and two desorption peaks for CO at 1000K and 1250K. The higher temperature CO peak is displaced to higher temperatures for low surface coverages and certain peaks may be absent for specific oxidants and/or gasification temperatures. These desorption peaks occur at similar temperatures for the different oxidants, and the principal differences between the spectra in Figures 1 through 5 lie in the intensity of the peaks. The general features of TPD spectra have been discussed by Hall and Calo [3], and are most clear for the O_2 oxidized char. The low temperature CO_2 peak appears to be at least partially the desorption of intrinsic CO_2-producing groups, most probably lactones and/or acid anhydrides [1, 4]. The higher temperature CO_2 peak has been shown to be at least partially due to secondary reactions of CO (gas) with non-desorbed surface complexes by via the reaction:

$$CO + [C\text{-}O] <=> CO_2 + C_f \qquad [R.1]$$
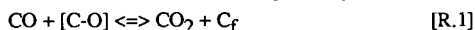
where [C-O] is a surface oxygen complex and C_f is an unoccupied active site. The 1000K CO

peak seems to be the result of intrinsic CO-producing groups such as carbonyls or semi-quinones. The origin of the 1250K peak (visible as a shoulder on the main CO peak in Figure 1) has been speculated to be at least partially due to the re-adsorption of CO to form a more stable CO surface complex [3].

The question that naturally arises then is whether the apparent uniformity in the chemical nature of functional groups can be used as a basis for a unified model of carbon gasification. At least part of the answer may be provided by a comparison of the relative reactivities, TPD spectra and surface area measurements of the same char gasified by NO, O_2, and CO_2.

Table 1 shows degree of burn-off, reactivity, total amount of oxygen present as stable complex (i.e., $CO + 2CO_2$) desorbed during TPD, and the corresponding N_2 BET surface area of the resulting chars for the O_2, NO and CO_2 gasified chars.

There are a number of obvious differences between the oxidation behaviour of O_2 and NO. O_2 is more reactive than NO, and the rate of increase of reactivity of O_2 with temperature in the low temperature range (< 900K) is also greater. For comparable O_2 and NO reactivities, (i.e., NO at 1123K and O_2 at 723K), the O_2 gasification surface area is over 20 times greater than the NO gasified surface area. This is indicative of significant porosity development in O_2 and that the reaction is restricted to "external"surface area in NO. This is confirmed by the CO_2 surface areas being lower than, or of the order of, the N_2 surface areas. The fact that the O_2 gasification surface area at 723K is also greater than the 723K NO gasification surface area implies that this is not simply a thermal effect. Further evidence for this comes from the fact that the N_2 surface area, and the amount of stable complex, as determined by the TPD experiments, does not vary with degree of NO gasification at 723K. Table 1 shows that both surface area and amount of stable complex are strong functions of degree of burn-off for O_2 gasification.

Another significant difference between the O_2 and NO-gasified chars can be discerned from the TPD spectra of the chars in Figures 6 and 7, respectively. The higher temperature CO peak is more intense than the 1000K peak for all of the NO-gasified chars, which may be interpreted as suggesting that there are few surface carbonyl or semi-quinone groups, or, at least, that they are of a different nature than those formed by O_2. There is also evidence for a 1000K shoulder for the 723K gasified chars, but, in the case of the 10% gasified char, this appeared following over 50 hours of exposure to NO. Only the mildest oxidation conditions, (e.g., chemisorption of NO at 523K), shown in Figure 3, produces a resolved low temperature CO peak. Conversely, the 1000K

peak is generally stronger than the 1250K peak for the O_2-gasified chars, and only for the 823K gasified chars are the peaks of comparable intensity.

Based upon the available evidence thus far, the absence of the less stable carbonyl or semi-quinone oxygen complexesin NO gasification may be accounted for by a fast reaction such as "stripping":

$$NO + C[O] \rightarrow CO_2 + 1/2\ N_2\ (or\ C-N) \qquad [R.2]$$

The limiting step in NO gasification could then be the formation of surface complexes by NO, which would tend to make the reaction first order with respect to NO. Indeed, first order kinetics have been reported for this reaction in a number of studies [5]. The NO "stripping" reaction can explain the origin of CO_2 in NO oxidation, which has previously been attributed to surface complex stripping by CO [5]. Vastola *et al.* [6] and Hall and Calo [3] have shown that the latter reaction does not take place appreciably under isothermal conditions. The higher temperature CO peak can be explained by the re-adsorption of bulk phase CO product from the reaction, since the gasification was conducted in a batch mode.

The preceding discussion still begs the question as to whether there is a causal relationship between the apparent absence of carbonyl or semi-quinone oxygen and the absence of porosity. An answer to this is necessarily speculative but, if indeed the gasification is adsorption-limited (due to relatively fast NO stripping and slow formation of complexes), then the equilibrium concentration of surface complexes would be less than for the corresponding O_2 gasification. The effectiveness of R.2 would also mean that NO has a low probability of significantly developing porosity. The result is that gasification would tend to proceed more in a "shrinking sphere" mode. For oxygen gasification, the situation is more complex. A larger fraction of the surface is covered by stable complex because there is no obvious "stripping" mechanism, and one molecule of O_2 can produce two complexes. Such effects as changes in the surface energetic heterogeneity with coverage, due to lateral complex-complex interactions, and limited accessibility of active sites result in more complex kinetics.

CO_2 has a much lower reactivity than NO, and Figure 2 shows that the principal desorption product after gasification at 1133K is high temperature CO. There is also, however, some evidence for 1000K CO. Unlike NO, CO_2 gasification develops measurable porosity in the Pittsburgh # 8 char. The absence of significant 1000K CO is most easily explained by the high gasification temperature (i.e., the high thermal decomposition rate of the resultant complexes) since, presumably, the 1000K sites are those directly involved in gasification. Results on other coal chars and carbons ([1, 2]) of non-gasifying CO_2 chemisorption show that both 1000K and

higher temperature CO are desorption products under these conditions. The generally low reactivity of chars in CO_2 can be explained by the hypothesis that upon dissociation, the products are a carbonyl or semi-quinone group and CO, both of which form stable complexes, thereby tending to stabilize the surface. The primary difference between O_2 and CO_2 gasification in the context of this qualitative model is that in O_2 adjacent carbonyl groups can interact to form less stable groups [4], whereas in CO_2 there is a significantly lower probability of having adjacent carbonyl or semi-quinone groups.

Conclusions

The theory of the unified nature of carbon-oxygen complexes seems to be qualitatively corroborated by the current work with different oxidizing agents. It has also been shown that commonality of functional groups, although of significance, is not sufficient to explain differences in reactivity or the manner in which gasification develops porosity. In particular, the rate of oxidant adsorption, the thermal stability of the dissociation products, and, in the case of NO oxidation, the possibility of oxygen stripping reactions, must also be taken into account. The use of an essentially non-porous char has shown that different oxidants can develop porosity quite differently in chars. The same may not be possible for some porous carbons due to the possibility that a relatively small degree of burn-off can produce significantly disproportionate porosity by opening previously inaccessible pores.

Acknowledgements

References

1. Marchon, B., Carrazza, J., Heinemann, H. and Somorjai, G.A. *Carbon*, **28**, 507, 1988.
2. Hall, P.J. and Calo, J.M. *Proc. Int . Carbon Conf. Carbon '88*, p.77, (McEnaney, E. and Mays, T.J., eds) IOP Publishing Co. Bristol, UK, 1988.
3. Hall, P.J. and Calo, J.M. submitted to *Energy and Fuels.*, 1988
4. Otake, Y. PhD Thesis, The Pennsylvania State University, 1986.
5. Chan, L.K., Sarofim, A.F. and Beer, J.M. *Combustion and Flame*, **52:37-45**, 37, 1983.
6. Vastola, F.J., Hart, P.J. and Walker, P.L., Jr, *Carbon*, **2**, 65, 1965.

Table 1, Reactivity and surface areas of
Pittsburgh # 8 coal char in various oxidants

Oxidant	Gasification Temperature, K	% Burn-off	Reactivity (g/g hr)	Total oxygen	N_2 Surface Area (m^2/g)
O_2	723	10	0.28	0.282	91
O_2	723	25	0.28	0.366	150
O_2	773	27	0.65	0.251	69
O_2	823	25	2.58	0.115	--
NO	723	5	3.3×10^{-3}	0.195	10
NO	723	10	3.2×10^{-3}	0.198	10
NO	923	10	3.5×10^{-2}	0.123	3
NO	1123	10	0.43	0.078	2
CO_2	1133	9	0.18	0.086	72
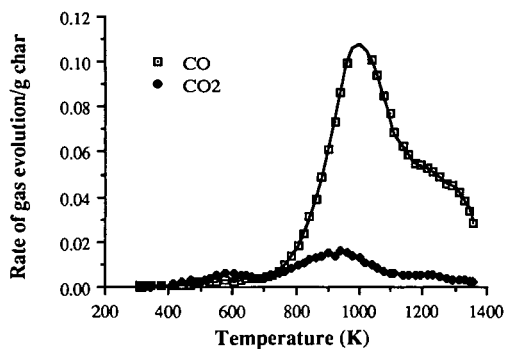
Figure 1. 100K/min TPD spectra of Pittsburgh # 8 coal char following gasification in 0.1 MPa of O_2 at 723K to 25% burn-off.

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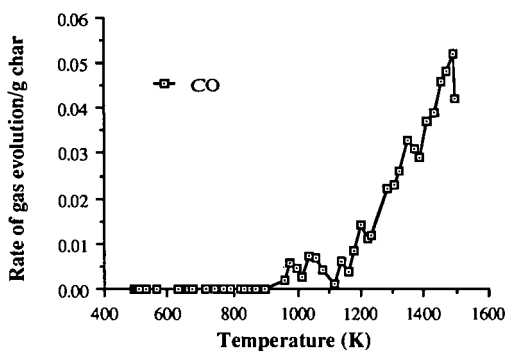
Figure 2. 100K/min TPD spectrum of Pittsburgh # 8 coal char following gasification in 0.1 MPa of CO_2 at 1133K to 9% burn-off.
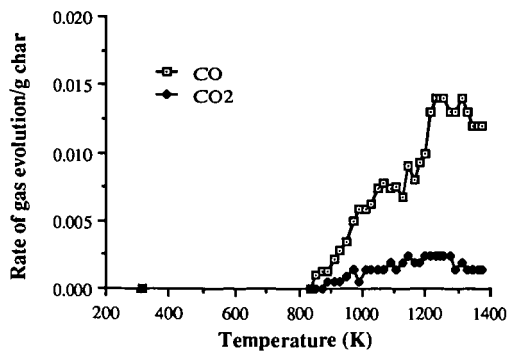

Figure 3. 100K/min TPD spectra of Pittsburgh # 8 coal char following chemisorption in 0.1 MPa of NO for 35 hours at 523K.
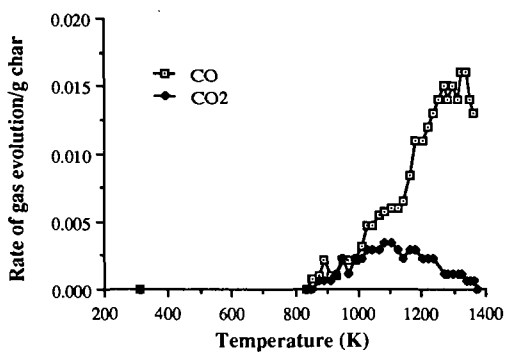
Figure 4. 100K/min TPD spectra of Pittsburgh # 8 coal char following oxidation in 15N HNO_3 for 0.5 hours at 323K.
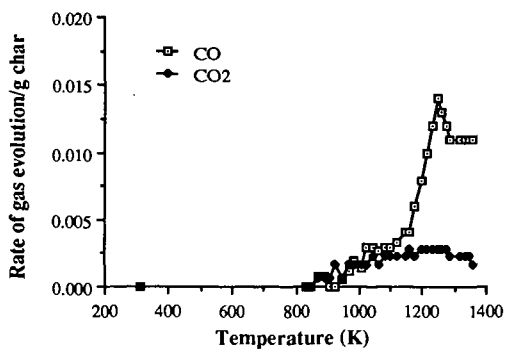

Figure 5. 100 K/min TPD spectra of Pittsburgh # 8 coal char following oxidation in H_2O_2 for 2 hours at 290K.
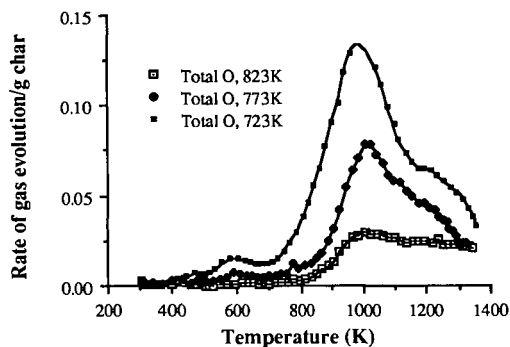
Figure 6. 100K/min TPD spectra of Pittsburgh # 8 coal char following gasification in 0.1 MPa O_2 to 25% burn-off at varying temperature.
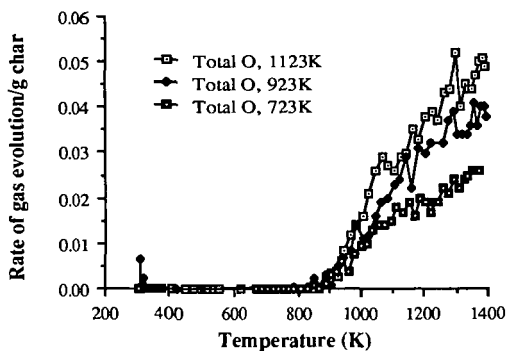

Figure 7. 100K/min TPD spectra of Pittsburgh # 8 coal char following gasification in 0.1 MPa NO to 10% burn-off at varying temperature.